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(54) **Rubber composition and tire using the same**

(57) The present invention provides a rubber composition with superior balance in abrasion resistance, processability, rolling resistance, and wet skid performance, and a tire using this rubber composition for the tread. A rubber composition comprising at least one rubber selected from the group consisting of diene rubbers and natural rubber, and per 100 parts by weight of the

rubber, 30 to 120 parts by weight of silica, and 5 to 40 parts by weight of zirconium silicate having an average particle diameter of at most 10 μm is used as a rubber composition for the tire tread. In addition, a tire tread is made from this rubber composition, and using this tread, a tire is manufactured.

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Description

[0001] The present invention relates to a rubber composition and tire made from this rubber composition. More specifically, it concerns a rubber composition for a tire tread, with superior balance in tire processability, rolling resistance, and wet skid performance, and a tire with a tread made from this rubber composition.

[0002] In recent years, global consciousness regarding resource and energy conservation has risen, and in the automobile industry, research is actively being conducted on a low fuel consumption tire with reduced rolling resistance in order to economize fuel consumption. One effective method of reducing the rolling resistance of a tire is the method of replacing some or all of the carbon black which has conventionally been used as a reinforcing agent, with silica. However, as demands toward tires rise, corresponding simply by the method of using silica is no longer satisfactory, and there is a need for further improvement in performance.

[0003] Besides low fuel consumption, a wide range of properties is requested in an automobile tire, such as wet skid performance, abrasion resistance, and processability, and various ingenious attempts are being made.

[0004] For example, for the purpose of improving wet skid performance, there is a prior art of compounding metal silicate with the rubber composition (JP-A-2001-40143). However, this stops short of fulfilling various other functions such as abrasion resistance, rolling resistance and processability.

[0005] The object of the present invention is to provide a rubber composition with superior balance in processability, rolling resistance, and wet skid performance, and a tire made from this rubber composition.

[0006] The present invention relates to a rubber composition comprising at least one rubber selected from the group consisting of diene rubbers and natural rubber, and per 100 parts by weight of said rubber, 30 to 120 parts by weight of silica, and 5 to 40 parts by weight of zirconium silicate having an average particle diameter of at most 10 μm .

[0007] The invention also concerns a tire with a tread made from the aforesaid rubber composition.

[0008] The present invention is explained in detail below.

[0009] The rubber composition of the present invention comprises a rubber component, silica, and zirconium silicate.

[0010] The aforesaid rubber component is diene rubber and/or a natural rubber. Examples of diene rubber are for example, styrenebutadiene rubber, butadiene rubber, isoprene rubber and the like, and mixtures of these may also be used.

[0011] Though there are no limitations as to the silica, dry process silica (silicic anhydride), wet process silica (silicic hydrate) and the like may be used. Of these, wet process silica is preferred. Preferable examples of wet process silica are Ultrasil VN3 (product name) available from Degussa Co., Nipsil VN3 AQ (product name) available from Nippon Silica Industrial Co., Ltd.

[0012] AS the silica, for example, silica with a nitrogen adsorption specific surface area (N_2SA) of 50 to 300 m^2/g can be used in the composition. When the N_2SA of silica is less than 50 m^2/g , the dispersion modifying and reinforcing effects tend to diminish, and when the N_2SA of silica exceeds 300 m^2/g , dispersion becomes poor and the heat build-up tends to increase.

[0013] The amount of silica to be compounded is 30 to 120 parts by weight, more preferably 40 to 90 parts by weight, most preferably 45 to 80 parts by weight, based on 100 parts by weight of the rubber component. When the amount of silica is less than 30 parts by weight, wet skid performance and reinforcing property diminish, and when the amount of silica is greater than 120 parts by weight, viscosity becomes high when kneading, and workability decreases.

[0014] It is preferable that the zirconium silicate is fine powder and the average particle diameter is at most 10 μm , preferably at most 2 μm . When the average particle diameter of zirconium silicate is greater than 10 μm , abrasion resistance and cut chipping performance diminish.

[0015] The amount of zirconium silicate to be compounded is 5 to 40 parts by weight, preferably 8 to 30 parts by weight, more preferably 10 to 20 parts by weight, based on 100 parts by weight of the rubber component. When the amount of zirconium silicate is less than 5 parts by weight, sufficient effects cannot be attained, and when the amount of zirconium silicate is greater than 40 parts by weight, abrasion resistance decreases.

[0016] In the present invention, by using silica and zirconium silicate together, in comparison to using them alone, the effect of improved balance between abrasion resistance, rolling resistance and wet skid performance can be attained.

[0017] In the rubber composition of the present invention, a silane coupling agent may also be compounded in joint use with silica.

[0018] Examples of silane coupling agents include bis(triethoxysilylpropyl)tetrasulfide, bis(triethoxysilylpropyl)disulfide, triethoxysilylpropylisocyanate, vinyltriethoxysilane, vinyltrimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -glycidoxypolypropylmethyldiethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -(polyethylene amino)-propyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N'-vinylbenzyl-N-trimethoxysilylpropylethylene diamine salt and the like. Among them, bis(triethoxysilylpropyl)tetrasulfide, bis(triethoxysilylpropyl)disulfide, triethoxysilylpropylisocyanate and γ -mercaptopropyltrimethoxysilane are preferable. And bis(triethoxysilylpropyl)disulfide is more preferable.

[0019] The amount of the silane coupling agent to be compounded is preferably 4 to 14 % by weight, more preferably 6 to 10 % by weight, based on the amount of silica. When the amount of the silane coupling agent is less than 4 % by weight, abrasion resistance and wet skid performance tend to decrease, and when the amount of the silane coupling agent is greater than 14 % by weight, the improvement of physical properties is small despite an increase in costs.

[0020] Furthermore, aside from the rubber component, silica, zirconium silicate and silane coupling agent, a compounding agent which is generally used in the rubber composition, such as carbon black, process oil, zinc oxide, wax, antioxidant, vulcanizing agent, or vulcanization accelerator may be compounded accordingly to the rubber composition of the present invention.

[0021] The rubber composition of the present invention is obtained by mixing the rubber component, silica, zirconium silicate, and any other compounding agents, as the need arises, by using the usual processing machine, such as a roll, Banbury mixer, kneader and the like.

[0022] The tire of the present invention is prepared by using the aforesaid rubber composition as a tire tread, according to the conventional method. Specifically, the rubber composition, when still unvulcanized, is processed by extrusion into the form of the tire tread, each tire part being laminated together on the tire making machine in the conventional method, to form an unvulcanized tire. A tire is then obtained by heating and pressurizing these unvulcanized tires in the vulcanizer. The tire obtained in this way has an excellent balance of processability, rolling resistance, and wet skid performance.

EXAMPLES

[0023] The present invention is explained in detail based on Examples below, but not limited thereto. In Examples and Comparative Examples, the following materials are used.

Natural rubber: RSS #3

S-SBR: Nipol NS116R available from Zeon Corporation. (amount of styrene unit: 20 % by weight, amount of 1,2-diene unit: 60 % by weight)

Silica: Zeosil 1165MP available from Rhoia Co., Ltd.

Zirconium silicate: Micropacks SS available from Hokusui Tech Co., Ltd. (average particle size: 2 μ m or less in 100 %)

Silane coupling agent: Si69 available from Degussa Co.

Process oil: Diana Process AH 40 available from Idemitsu Kosan Co., Ltd.

Zinc oxide: Zinc Oxide No. 2 available from Mitsui Mining and Smelting Co., Ltd.

Wax: SUN NOC wax available from Ohuchi Shinko Kagaku Kogyo Co., Ltd.

Stearic acid: KIRI available from NOF Corporation

Antioxidant: Santoflex 13 ((N-1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) available from FLEXSYS CO.

Sulfur: sulfur available from Karuizawa Seirensheo Kabushiki Kaisha.

Vulcanization accelerator CBS: Nocceler CZ-G (N-cyclohexyl-2-benzothiazolylsulfenamide) available from Ohuchi Shinko Kagaku Kogyo Co. Ltd.

Vulcanization accelerator DPG: Soxinol D (diphenyl guanidine) available from Sumitomo Chemical Co., Ltd.

EXAMPLES 1 to 2 and COMPARATIVE EXAMPLES 1 to 3

Processing method

[0024] The raw material rubber and materials to be compounded except for sulfur and vulcanization accelerator were mixed by using a Banbury internal mixer, based on the compounding recipe shown in Tables 1 and 2. Sulfur and vulcanization accelerator were then added to the obtained masterbatch on an open roll to prepare the rubber composition for the tire tread. Subsequently, the respective rubber compositions of Examples 1-2 and Comparative Examples 1-3 were used as the tread of pneumatic tires, and the following property evaluations were carried out.

(Rolling resistance)

[0025] The rolling resistance was measured according to the usual method under the conditions of a load of 4.66 kN, an inner pressure of 200 kPa and a speed of 80 km/hour. The rolling resistance was represented as an index to the value of Comparative Example 1 as 100 according to the following equation (rolling resistance index). The larger the index, the smaller the rolling resistance is and the better the property is.

$$(\text{rolling resistance index}) = (\text{rolling resistance value of}$$

Comparative Example 1) ÷ (rolling resistance value of Example or

Comparative Example) × 100

(Wet skid performance)

[0026] The braking distance from the initial running speed of 64 km/h was measured on a wet asphalt road. In the test, a Japanese front engine/front wheel drive automobile with a tire size of 185/65R14 was used. The wet skid performance was represented as an index to the value of Comparative Example 1 as 100 according to the following equation (wet skid index). The larger the index, the more excellent the wet skid performance is.

(wet skid index) = (braking distance value of Comparative

Example 1) ÷ (braking distance value of Example or Comparative

Example) × 100

(Abrasion resistance)

[0027] A tire with the obtained tread was installed on a Japanese front engine/front wheel drive automobile. After the automobile was run for 15,000 km on a paved road, the driven distance at which the tire tread is worn out by 1 mm was compared, and the value was represented as an index to the value of Comparative Example 1 as 100 according to the following equation (abrasion resistance index). The larger the index, the more excellent the abrasion resistance is.

(abrasion resistance index) = (value of distance driven in

Example or Comparative Example) ÷ (value of distance driven in

Comparative Example 1) × 100

[0028] The results are shown in Table 2.

[0029] In comparison to Comparative Example 1, in which zirconium silicate was not compounded into the silica compounded rubber composition, and Comparative Example 2, in which a small amount of zirconium silicate was compounded, the balance between abrasion resistance, processability, wet skid performance and rolling resistance was improved in Examples 1-2, in which the appropriate amount of zirconium silicate was compounded.

[0030] On the other hand, in Comparative Example 3, in which a great deal of zirconium silicate was compounded, although rolling resistance and wet skid performance increased, abrasion resistance and processability diminished considerably.

TABLE 1

Materials	Part by weight
Natural rubber	30
S-SBR	70
Silica	Variable
Zirconium Silicate	Variable
Silane coupling agent	6.4
Process oil	22
Zinc oxide	2.5
Wax	1
Stearic acid	2
Antioxidant	1.5
Sulfur	1.5
Vulcanization accelerator CBS	1.5

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TABLE 1 (continued)

Materials	Part by weight
Vulcanization accelerator DPG	1

TABLE 2

	Ex.		Com. Ex.		
	1	2	1	2	3
Silica	75	70	80	80	60
Zirconium Silicate	10	20	-	3	45
Rolling resistance	102	105	100	100	115
Wet skid performance	101	103	100	100	105
Abrasion resistance	102	98	100	100	84

[0031] According to the present invention, by compounding a specific amount of silica and zirconium silicate to the rubber composition, the balance between tire processability, abrasion resistance, rolling resistance, and wet skid performance can be improved compared to prior technology.

Claims

1. A rubber composition for a tire tread comprising:

at least one rubber selected from the group consisting of diene rubbers and natural rubber, and per 100 parts by weight of said rubber,
30 to 120 parts by weight of silica, and
5 to 40 parts by weight of zirconium silicate having an average particle diameter of at most 10 μm .

2. A tire with a tread comprising the rubber composition of Claim 1.



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EUROPEAN SEARCH REPORT

Application Number
EP 02 02 8344

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
D,X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 19, 5 June 2001 (2001-06-05) -& JP 2001 040143 A (SUMITOMO RUBBER IND LTD), 13 February 2001 (2001-02-13) * abstract *	1,2	C08L7/00 C08L9/00 C08K3/00 C08K3/08 C08K3/34 C08K3/36 B60C1/00
Y	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 14, 5 March 2001 (2001-03-05) -& JP 2000 319447 A (SUMITOMO RUBBER IND LTD), 21 November 2000 (2000-11-21) * abstract *	1,2	
Y	EP 0 928 810 A (SUMITOMO RUBBER IND) 14 July 1999 (1999-07-14) * claim 1; examples *	1,2	
Y	US 5 821 290 A (LABAUZE GERARD) 13 October 1998 (1998-10-13) * claims 1,7,15; example 3 *	1,2	
Y	US 5 069 816 A (DESANTIS DOMINICK A ET AL) 3 December 1991 (1991-12-03) * page 11, column 19, line 56 - page 11, column 19, line 62 *	1,2	C08L C08K B60C
Y	WO 00 73372 A (MICHELIN RECH TECH ;MICHELIN SOC TECH (FR); SIMONOT LAURE (FR); CU) 7 December 2000 (2000-12-07) * claims 1,8,16 *	1,2	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 6 February 2003	Examiner Schmitz, V
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 02 8344

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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06-02-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2001040143 A	13-02-2001	NONE	
JP 2000319447 A	21-11-2000	NONE	
EP 0928810 A	14-07-1999	JP 11181153 A	06-07-1999
		EP 0928810 A2	14-07-1999
		US 6184283 B1	06-02-2001
US 5821290 A	13-10-1998	AT 220414 T	15-07-2002
		AU 721437 B2	06-07-2000
		AU 6795296 A	10-04-1997
		CA 2174485 A1	05-04-1997
		CN 1148606 A ,B	30-04-1997
		DE 69622235 D1	14-08-2002
		DE 69622235 T2	23-01-2003
		EP 0767206 A1	09-04-1997
		ES 2178687 T3	01-01-2003
		JP 9111051 A	28-04-1997
US 5069816 A	03-12-1991	NONE	
WO 0073372 A	07-12-2000	AU 5525100 A	18-12-2000
		BR 0006169 A	17-04-2001
		CA 2338162 A1	07-12-2000
		CN 1318083 T	17-10-2001
		WO 0073372 A1	07-12-2000
		EP 1114093 A1	11-07-2001
		US 2002004549 A1	10-01-2002

EPO FORM P0655

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

